

Thermodynamic relations for DNA phase transitions

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Abstract: The force induced unzipping transition of a double stranded DNA is considered from a purely thermodynamic point of view. This analysis provides us with a set of relations that can be used to test microscopic theories and experiments. The thermodynamic approach is based on the hypothesis of impenetrability of the force in the zipped state. The melting and the unzipping transitions are considered in the same framework and compared with the existing statistical model results. The analysis is then extended to a possible continuous unzipping transition.

Keywords: DNA unzipping; Melting and force induced transitions; Thermodynamic relations

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1. Introduction

To read the genetic information encoded in the base sequence, hidden in the helical structure of a DNA, it is necessary to break the hydrogen bonds of the base pairs [1]. The mechanism for doing so is the unzipping by a force [2, 3] of a double stranded DNA (dsDNA), or a thermal melting [4, 5]. In the melting transition, the hydrogen bonds of base pairing are broken by thermal energy, while in the unzipping transition, it is by a pulling force at one end of the DNA. In both cases, the strands remain intact.

While there is a long history of experimental studies of the melting transition [4, 5], the investigations of the unzipping transition or responses to external forces are of more recent origin [6]. Pioneering calorimetry studies have been done over a large range of temperature (T) from 2 to 400 K under different solution conditions [7]. So far as force is concerned, isotherms of DNA, like the response under a force have been obtained in many different types of single molecule experiments [8–10]. However, calorimetry in presence of a force is still not available.

It is known from various theoretical models that, for both melting and unzipping, the nature of the transition depends on the aspects of the DNA captured in a model

[2, 8, 11–20]. Any natural DNA, because of its large length, is expected to show the characteristic features of the transitions, but the situation is not so clear on the experimental front. Since experiments are restricted to very short chains, it is not clear if the predicted transition varieties are at all seen with variations in the base sequence, as for example, across species, or there is actually only one type. We even lack a clear experimental answer about the order of the melting transition.

Cooperativity in melting comes from the entropy (S) of the DNA through the correlations introduced by the strands as long polymers [21, 22]. The unzipping transition is due to the competition between the pairing of the strands and the stretching of the unbound strands [2, 11–13]. The work done in stretching the free polymers provides the cost of unpairing the strands. This cost at zero temperature is only the pairing energy, but, because of entropy, the critical unzipping force vanishes as one approaches the melting temperature. The thermodynamic conjugate pair for the transition is g , the unzipping force, and x , the separation of the two strands at the point of application of force (see Fig. 1). It transpires that gross quantities like the entropy, the specific heat, and the response function for force, are the relevant thermodynamic quantities to study, especially as the transition point is approached. The advantage in the thermodynamic approach is that the results obtained are valid under quite general conditions without getting into the microscopic details of DNA.

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The constant force specific heat is given by

$$C_A = T \left. \frac{\partial S_A}{\partial T} \right|_g. \quad (38)$$

The derivative of the entropy can be expressed in terms of the derivative along the transition line as

$$\frac{dS_A}{dT} = \left. \frac{\partial S_A}{\partial T} \right|_g + \left. \frac{\partial S_A}{\partial g} \right|_T \frac{\partial g^*}{\partial T}, \quad (39)$$

and a similar relation for phase B. Since at each point on the transition line entropy is continuous, $\frac{dS_A}{dT} = \frac{dS_B}{dT}$. Equation (38) can now be used to express the constant force specific heat difference as

$$C_A - C_B = T \left. \frac{\partial g^*}{\partial T} \right|_T \left[\left. \frac{\partial S_A}{\partial g} \right|_T - \left. \frac{\partial S_B}{\partial g} \right|_T \right]. \quad (40)$$

A further simplification can be achieved by using one of the Maxwell relations, Eq. (34d),

$$\left. \frac{\partial S_A}{\partial g} \right|_T = \left. \frac{\partial S_A}{\partial x} \right|_T \left. \frac{\partial x}{\partial g} \right|_T = \frac{\partial g^*}{\partial T} \chi_A, \quad (41)$$

where χ_A is the extensibility of phase A. With a similar relation for phase B, we obtain

$$C_A - C_B = -T \left(\frac{\partial g^*}{\partial T} \right)^2 (\chi_A - \chi_B). \quad (42)$$

If the extensibility of phase A is less than that of B, then the specific heat of phase A is higher than that of B.

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